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Ionic and excited species in irradiated poly(ethylene terephthalate) doped with pyrene

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Abstract

Temperature effect on the fate of ionic and excited species in stationary irradiated poly(ethylene terephthalate), doped with pyrene, were examined using wavelength selected radiothermoluminescence and absorption spectroscopic methods. In general, all intermediates were found to disappear at temperatures higher than ~180 K. Some small fraction of pyrene radical cations was still detected in temperatures close to room ones. The relaxation phenomena in this polymeric matrix certainly stimulated the behaviour of all intermediates trapped in the system. The detailed mechanism of reactions involved was proposed.

Keywords: Electron beam irradiation; Radiothermoluminescence; Ion recombination; Relaxation phenomena; Poly(ethylene terephthalate); Pyrene

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most widely used industrial polymer material. Detailed knowledge concerning the structures and physical properties of the polymer is indispensable for its applications in microelectronics, optics, packaging techniques and medical areas.

The nature of the excited state interactions in PET is still the subject of discussions [1–14]. In photochemical terms, the interactions between the carbonyl groups and the aromatic ring make PET a much more complex system than polystyrene or poly(methyl methacrylate). Basic structural unit of this polymer can be treated as an example of a bichromophoric system. The aromatic ring in the chain backbone and the carbonyl groups adjacent to the backbone ring could lead to interactions that might result in monomer, excimer or exciplex states formation, depending on molecular group orientation and distance of polymer chains.

The spectral distribution of luminescence observed for electron beam irradiated PET film at room temperature [15,16] was found to be similar to that one obtained for photoexcited PET [1–14]. Luminescence observations extending over a long period of time after irradiation at low temperatures were carried out for PET by Hama et al. [17]. They attributed isothermal luminescence spectrum of PET observed at 83 K to emission from excited ester groups or *p*-phenylene ones. Those excited species were generated via the recombination of electron-cation pairs through electron tunnelling mechanism [17]. Thermoluminescence glow curves of PET were reported by Hama et al. [17] and Takai et al. [18] too.

We had investigated the transient species in pulse-irradiated PET in temperature range 30–295 K [16]. The electron transfer and radical ions recombination were found to be temperature dependent. The tunnelling mechanism at low temperatures (approximately $T \leq 170$ K) and relaxation induced charge transfer at higher ones were found to influence the recombination processes.

Recently, in our laboratory recombination processes in pure and pyrene doped polyethylene [19], polypropylene [20] and poly(methyl methacrylate) [21] have been investigated using wavelength selected radiothermoluminescence (WS RTL) technique. Pyrene (Py) can be used as a spectroscopic probe because its radical ions, radicals, triplet and singlet states are well characterized spectroscopically. In our investigations Py can help to identify the luminescence centres and to observe ionic events in the polymeric system.

The aim of this work is to find the correlation between the radioluminescence data of Py doped PET and the decay of ionic species observed by spectrophotometric absorption method in order to identify ionic processes leading to excited states generation. In particular the influence of Py on radiation induced events in PET–Py system at low temperature will be investigated.

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2. Experimental details

Poly(ethylene terephthalate) (PET) film, 100 μm thickness, stretched biaxially, was produced by Nitron Ltd., Krupski Młyn, Poland. Methanol (for spectroscopy, Uvasol, Merck) was used as received. Pyrene, Py (analytical grade, Sigma), was recrystalized twice from ethanol. The PET film strips were boiled in methanol for 3 h in order to remove low molecular impurities. Py was introduced into PET by boiling the previously purified polymer film in solution of Py in methanol. Afterward the polymer films were rinsed with methanol at room temperature to remove traces of Py from the surface. The concentration of Py in PET was determined spectrophotometrically using Hewlett-Packard HP8452A diode array spectrophotometer.

Polymer strips (5×100 μm thick) hold in copper frames were kept in the vacuum (10^{-4} Torr for 20 h) in order to remove oxygen and the solvent traces. Afterwards the samples were immersed in liquid nitrogen and irradiated using a linear accelerator (ELU-6, USSR made) which delivered 6–8 MeV electron pulses; 1 μs (dose ∼ 250 Gy) and 4 μs (dose ∼ 500 Gy) pulses were used. Total dose was kept in the range 2.5–6.5 kGy. The emission spectra and radiothermoluminescence curves at selected wavelength (WS RTL) were recorded using the equipment described previously [19]. During the WS RTL experiments the average heating rate was ca. 3.5 K min^{-1} in the temperature range 80–200 K. The optical absorption spectra were examined using the cryostate Optistat DN with temperature controller ITC 502 (Oxford Instruments Ltd.) using a Cary 5E spectrophotometer (Varian Ltd.). The time span between the start of absorption/emission measurements and irradiation was kept constant, i.e. 5 min. After that the sample was heated up to desired temperature than the absorption spectrum was taken at constant temperature (the spectrum scan rate was 2000 nm min^{-1}) and the procedure started again.

The short lived species were investigated using a linear electron accelerator (ELU-6, USSR made) and our pulse radiolysis system described earlier [16].

3. Results and discussion

3.1. Steady state radiolysis of PET doped with Py

The optical absorption spectra of PET pure and doped with Py irradiated at 77 K are presented in Fig. 1. All spectra were also recorded at 77 K. The absorption band with maximum at ca. 450 nm can be attributed to Py radical cation, $\text{Py}^{\bullet +}$, whereas two absorption bands with maxima at 374 nm and in the range 500–535 nm can be ascribed to PET radical ions [16]. The optical absorption spectra of irradiated at 77 K pure PET presented in Fig. 1, insert, were recorded during slow warming up of the sample from 77 K to room temperature. Comparing these results with the PET radical ion lifetimes found earlier [16] (for example at 115 K the 500–535 nm band decayed in microsecond time scale) one should conclude that during pulse radiolysis experiments photobleaching effect caused by analysing light should be considered. The photobleaching of radical ions (electrons) in frozen systems by intense light beam was observed previously [22,23]. Having in mind the results for PET–Py system shown in Fig. 1 two conclusions might be drawn: the strong Py concentration effect observed (the ratio of absorptions taken at ∼450 nm ($\text{Py}^{\bullet +}$) and at 535 nm (PET ions) equalled 0.57 and 1.3 for Py concentrations in PET 1.2×10^{-3} and 1.3×10^{-1} mol dm^{-3}, respectively) and the lack of $\text{Py}^{\bullet -}$ band at 495 nm. Although the electron affinity (EA) of PET seems to be unknown but taking into account the relative EA values in 2-methyltetrahydrofuran, (MTHF) glass found for phthalic anhydride, 1.24 eV and for Py, 0.63 eV [24] the electron transfer between $\text{PET}^{\bullet -}$ and Py seems to be impossible. If so, the 500–530 nm absorption band found in the presence of very high Py concentration should represent mainly $\text{PET}^{\bullet -}$ absorption.

The optical absorption spectra of irradiated at 77 K PET–Py system were investigated in temperature range 77–290 K. The temperature dependence of absorption band intensities at 374, 450 and 535 nm shown in Fig. 2 was analysed for different Py content in PET film. In temperature range 77–180 K absorption peaks recorded at 374 and 535 nm decreased in a similar way for lower Py concentration system (Fig. 2B) as for pure PET (insert B in Fig. 1). Close to the 180 K and above this temperature one can observe only absorption band with maximum at ca. 450 nm corresponding to Py radical cation. The traces of absorption band at 440–450 nm were recorded even at temperatures close to room one for PET containing of $\sim 1.3 \times 10^{-1}$ mol dm^{-3} Py. The long-lived $\text{Py}^{\bullet +}$ species in PMMA matrix were observed at room temperature [25]. In general, long lived dopant ionic species can be observed for systems which are active against primary ionic products (electrons and holes) of the matrix radiolysis.

The WS RTL curves recorded at 475 and 600 nm for PET containing Py irradiated at 77 K with dose 2 kGy are presented in Fig. 3A. Both curves showed the maxima at ca. 110 K as it was found for pure PET matrix (Fig. 3B). The intensity of the emission start to be very low in the temperature range higher than 180 K for pure and Py doped PET. The spectral distributions of PET–Py system luminescence recorded at 107 and 147 K exhibited two broad emission bands with maxima at 475 and 600 nm as it is shown in insert of Fig. 3A. In our WS RTL investigations of polymers doped with Py [19–21] we observed three luminescence bands with maxima at 395, 475 and 600–650 nm attributed to Py monomer, excimer fluorescence and Py phosphorescence, respectively. In the system under consideration the luminescence band designed to monomer fluorescence of Py at 395 nm was not detected (Fig. 3A).

The strong emission band observed in the range 600–650 nm certainly represent Py phosphorescence. One can expect that the Py excimer fluorescence should be

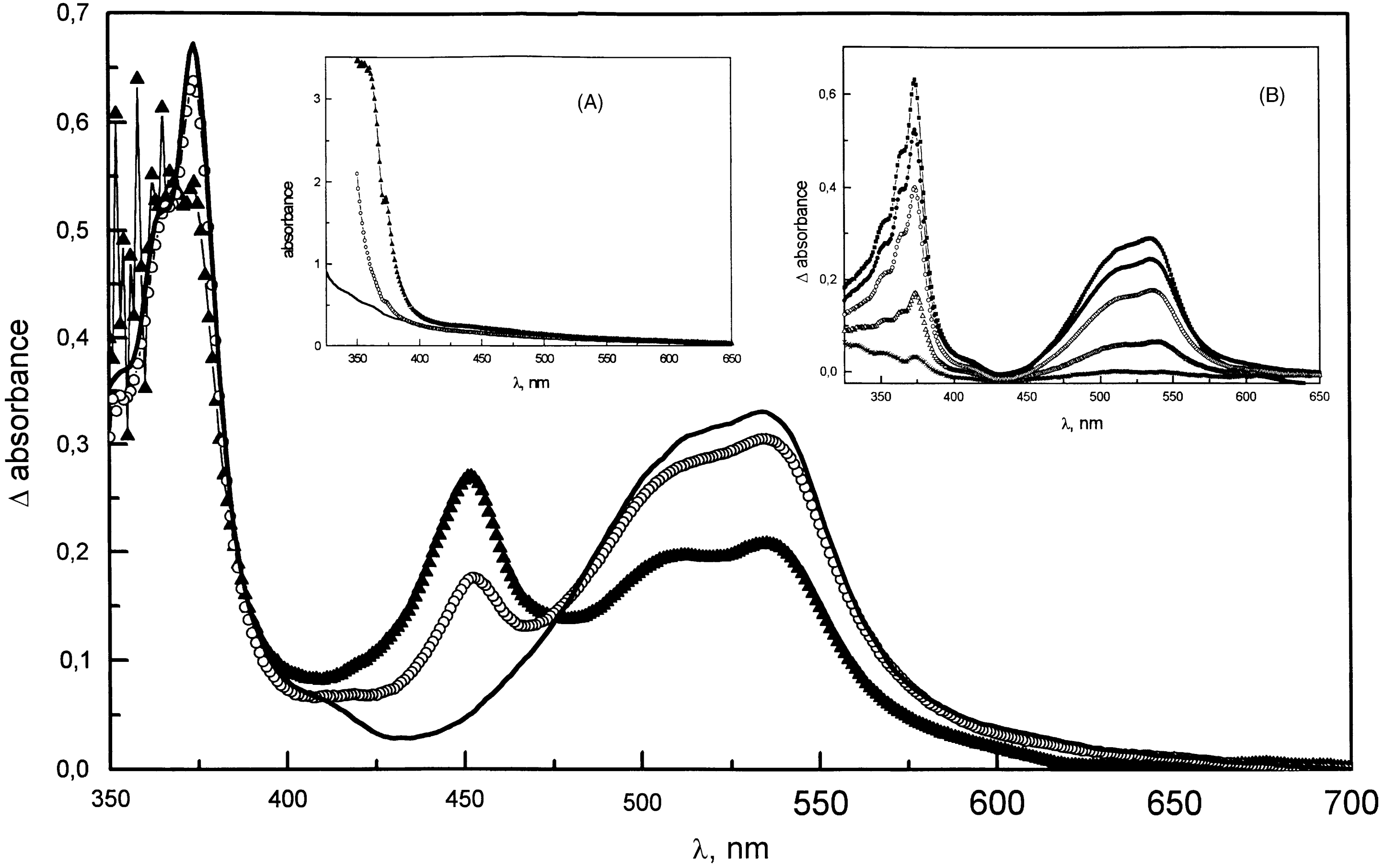

Fig. 1. The optical absorption spectra of pure PET (—), and PET containing Py: $\sim 1.2 \times 10^{-3}$ mol dm^{-3} (○); $\sim 1.3 \times 10^{-1}$ mol dm^{-3} (▲); irradiated at 77 K with dose 6.5 kGy, recorded at 77 K 5 min after the end of irradiation. Insert (A): the absorption spectra of non irradiated PET pure (—) and containing Py: $\sim 1.2 \times 10^{-3}$ mol dm^{-3} (○); $\sim 1.3 \times 10^{-1}$ mol dm^{-3} (▲). Insert (B): the influence of temperature on the optical absorption spectra of PET film irradiated at 77 K with dose 6.5 kGy and recorded at 77 K (■), 100 K (●), 120 K (○), 150 K (△) and 180 K (×). All spectra were corrected on absorption spectrum of non irradiated sample. The thickness of the PET films equalled 440 μm.

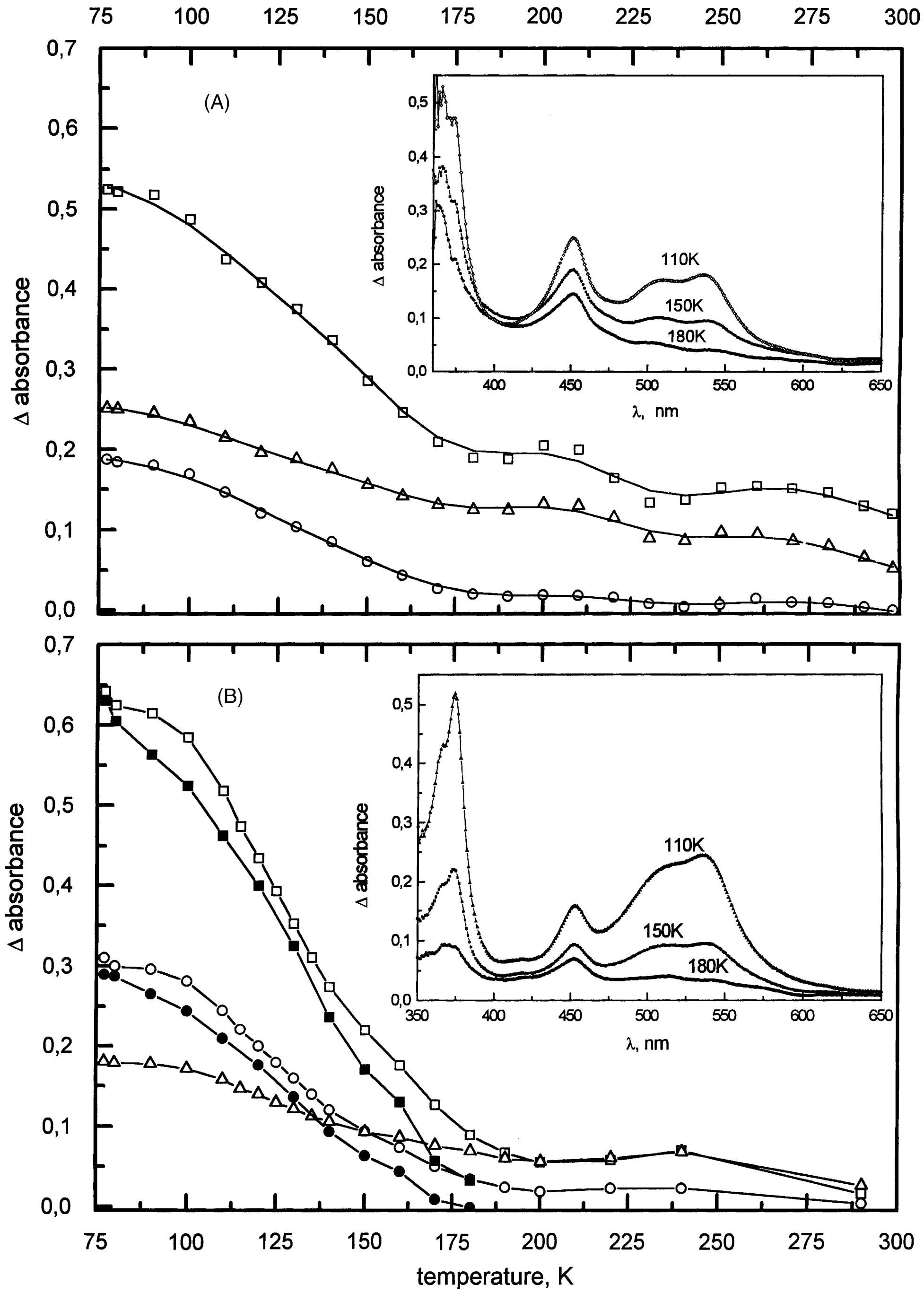

Fig. 2. The influence of Py concentration and temperature on the optical absorption spectra of PET film (440 μm thickness): (A), [Py] ~ 1.3×10^{-1} mol dm^{-3}; (B), [Py] ~ 1.2×10^{-3} mol dm^{-3}. Optical densities were recorded at 374 nm (☐), 452 nm (△) and 535 nm (○) for PET–Py systems irradiated at 77 K with dose 6.5 kGy. For comparison the data for PET film without Py (taken from insert B of Fig. 1) 374 nm (■), 535 nm (●) are also shown in Fig. 2B. The absorption spectra recorded at chosen temperatures are shown in inserts.

found as a emission band with λ_{max} ~ 475 nm. Comparing the spectral distribution of the emissions for PET–Py system (Fig. 3A) and for pure PET (Fig. 3B) it is seen that in both cases the 475–500 nm bands were found although for pure PET the maximum was lightly shifted towards longer wavelengths. May be this effect is due to the Py excimer fluorescence contribution originated from Py microcrystals formed for high Py content (~1.3×10^{-1} mol dm^{-3}) in PET. It was revealed by early experiments that the pyrene crystal shows excimer emission, without any monomer fluorescence [26]. It is reasonable that in PET–Py system, dopant molecules were introduced into amorphous region, their distribution was non-homogenous and one can expect local strong aggregation of Py molecules.

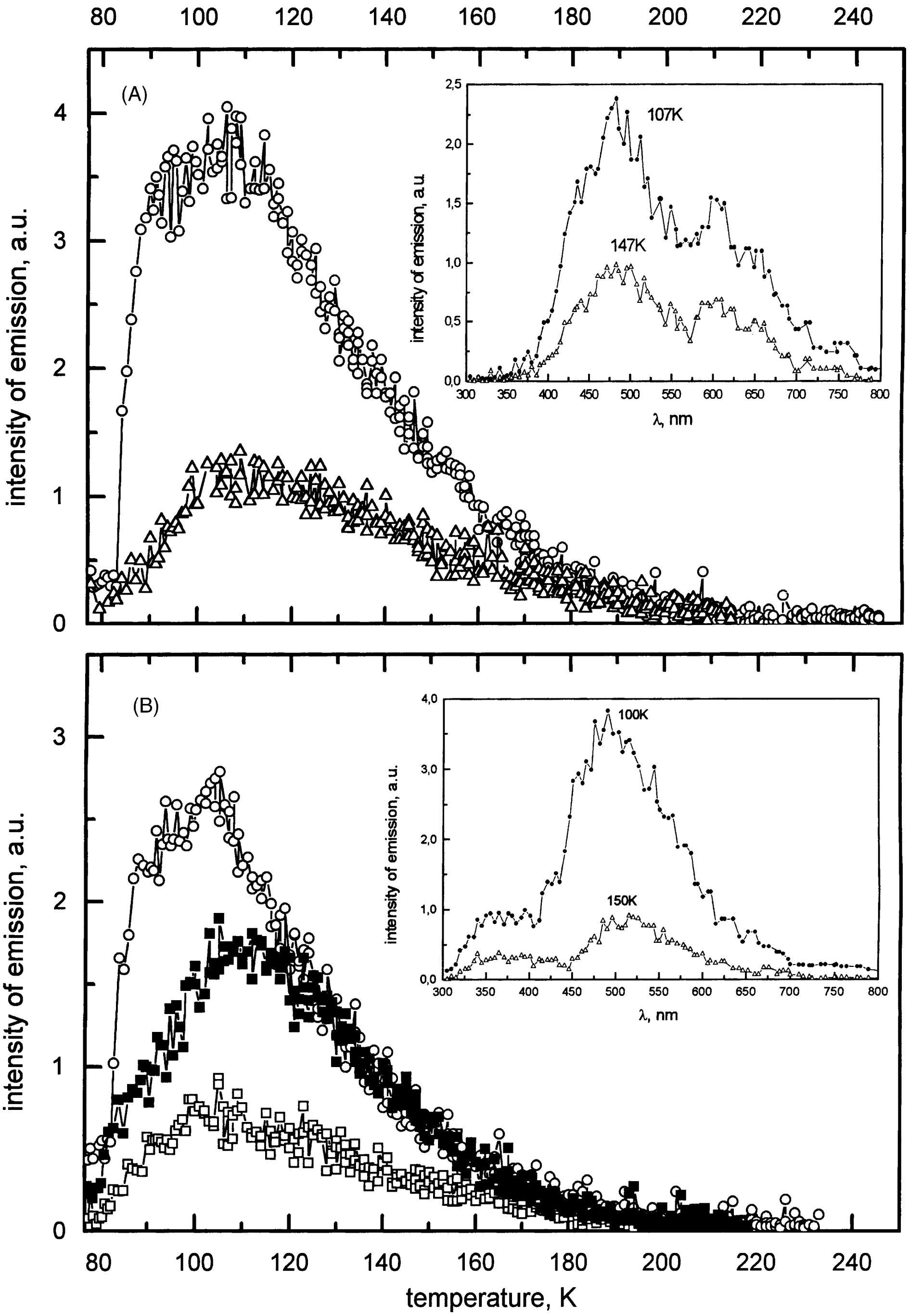

Fig. 3. (A) WS RTL curves recorded at 475 (○) and 600 nm (△) for PET film (70 μm thickness) containing ~1.3×10^{-1} mol dm^{-3} Py, irradiated with dose 2 kGy at 77 K. Insert: spectral distributions of radioluminescence for PET–Py (~1.3×10^{-1} mol dm^{-3}) system recorded at different temperatures. (B) WS RTL curves recorded at 370 (□), 475 (○) and 550 nm (■) for pure PET film (90 μm thickness) irradiated with dose 2 kGy at 77 K. Insert: spectral distributions of radioluminescence for PET film (100 μm thickness) recorded at different temperatures after irradiation at 77 K.

On the basis of pure PET photoexcitation studies [1–13] the 338 nm emission shown in Fig. 3B insert can be assigned to the fluorescence from the first excited singlet (π–π^*) state, whereas the 368 nm fluorescence may be attributed to an associated ground-state dimer of the terephthalate units. The first excited triplet state $^3(\pi$–$\pi^*)$ is responsible for the 464 nm phosphorescence, whereas the 564 nm phosphorescence may be assigned to the triplet state of associated dimer [11]. Tsumura et al. [27] investigating the radiothermoluminescence mechanism of aliphatic oligoesters, observed phosphorescence band in 450–500 nm wavelength region and they attributed it to *n*–π^* transition of ester group. It is worth to mention that emission band with maximum at 480–500 nm was observed at low temperatures for poly(methyl methacrylate) (PMMA) irradiated at 77 K [21] and it was assigned to deactivation of excited ester group in PMMA. Windhager et al. [28] reported phosphorescence emission spectrum of photochemically excited PMMA with maximum at 469 nm. Having in mind these all information concerning the pure PET radioluminescence, the PET–Py system should certainly represent much more complex system.

All WS RTL curves in Fig. 3 show the maxima in temperature range 100–115 K. Our WS RTL peaks are shifted towards lower temperatures comparing with Hama et al. [17] RTL-unfiltred light observations for PET irradiated by electron beam at 83 K. A correlation was found between our results and thermally stimulated current (TSC) data for PET [18]. Takai et al. [18] provided, that the TSC peak at 108 K was mainly due to dipole depolarisation and another peak around 173 K was induced by the released carriers which had been photogenerated and trapped under a poling field at 88 K.

Summing up, the radioluminescence and the ionic species responsible for light generation almost disappeared in temperatures higher than ∼180 K. Molecular relaxations in PET at low temperatures have been investigated by many workers, and their results were discussed by Takai et al. [18]. The β-relaxation in PET was ascribed to local motion of main chains, accompanied by movement of COO groups. Chemical structure of main chain and possibilities of COO group conformations in PET make this system disordered and space non-homogenous. The temperatures assigned to β-relaxation strongly depended on experimental method used. Two mechanical loss peaks at 168 and 203 K were ascribed to the molecular motion of COO groups [29]. At 173 K the TSC peak was detected [18]. Bell and Murayama [30] observed β-relaxation in PET at temperature range 213–233 K, and associated it with motions in the chain folds. We reported two temperature regions in temperature range 164–172 K and at 250 K for breakdown in Arrhenius dependences, for pulse radiolysis studies of PET transient species [16]. The onset of β-relaxation in PET in temperature range ∼165–175 K can be probably associated with rotation of COO groups, which destroyed extended conjugated π system (–OOC–C_6H_4–COO–). As a result, the luminescence followed the tunnelling of recombining ionic species located on terephthalate units disappeared. It is worth to note, that specific temperature dependence in temperature range 165–175 K was detected in charge transfer experiments [16,18].

3.2. Pulse radiolysis study

A pulse radiolysis study of PET film containing Py has been carried out with the main aim of investigating early stages of reactivity transfer processes in the system under consideration. The optical spectra of pulse-irradiated PET–Py system at 100 K are shown in Fig. 4. The strong absorption band with maximum at 415–420 nm can be assigned to the Py triplet states, $^3\text{Py}^*$ [31]. The other transient band at 520–530 nm can be attributed to PET radical ions by comparison with the spectrum of neat PET film [16]. In the same wavelength range the second absorption band of Py triplets was observed [31] and as result PET ionic species absorption, 500–530 nm may be disturbed (Fig. 4). The maximum corresponding to the $\text{Py}^{\bullet +}$ ($\lambda = 450$ nm) can be found, but radical anion $\text{Py}^{\bullet -}$ peak at $\lambda = 490$–500 nm overlapped the PET ionic species absorption (see arrows in the Fig. 4). The $\text{Py}^{\bullet +}$ absorption band observed at 100 K seems to decrease whereas the $^3\text{Py}^*$ absorption band (415–420 nm) slowly increase in the hundreds microsecond time scale (Fig. 4, insert a). At room temperature strong Py triplet absorption band (415–420 nm) was only observed. We estimated the Py triplet lifetimes as a reciprocal of first-order rate constant of absorption decay at 415 nm at temperatures 293 and 95 K as 0.34 and 1.15 s, respectively. The Py triplet lifetime in PET at temperature 293 K (0.34 s) is very close to the Py triplet lifetimes in PMMA at room temperature (0.4–0.44 s) as it was found by Kellogg and co-workers [32,33] using phosphorescence decay technique. These authors [33] reported the Py triplet lifetime in PMMA at 77 K as equal to 0.63 s. The rate of the $^3\text{Py}^*$ absorption decay at 415 nm was temperature dependent (Fig. 5). In general, the decay of Py triplet states can be satisfactorily approximated by the first-order kinetic equation in time range below 1 s (Fig. 5 insert). The Arrhenius plot shown in Fig. 5 can be characterized by two linear parts which intersect at ca. 220 K, which is close to the β-relaxation temperature estimated for PET by Bell and Murayama [30]. The Arrhenius dependence breakdown observed for decay of ionic species absorbing at 430 nm in pulse radiolysis of PET [16] was found at 250 K. Activation energies calculated from two linear regions of the Arrhenius plot (Fig. 5) were equal to 5.03 and 0.69 kJ mol^{-1} for temperatures higher than 220 K and below this temperature, respectively. Up to now, we did not find information on temperature influence on triplet lifetime or phosphorescence of aromatic admixtures in PET matrix. The temperature effects on the phosphorescence of aromatic hydrocarbons in PMMA have been investigated [32–35]. Typical Arrhenius plots for aromatic triplet lifetimes in PMMA [32] were similar to our results presented in Fig. 5, and the activation energies in the range 0.3–0.36 kJ mol^{-1} were calculated [32] for temperatures below 200 K. Various possible mechanisms for phosphorescence decay and a dynamic quenching mechanism by polymer matrices were discussed by Horie [34]. Although there are some discrepancies concerning participation of radiative and non-radiative processes in phosphorescence decay in PMMA, most authors [34,35] had agreed that phosphorescence intensity and lifetime data might be used to detect transitions in polymers.

Very week emission during the pulse was detected in the range 350–450 nm for pulse irradiated (17 ns pulse) PET + Py (1.3×10^{-1} mol dm^{-3} and less) systems with the tail extending up to ca. 60 ns. Self absorption effect can influence this emission experiments.

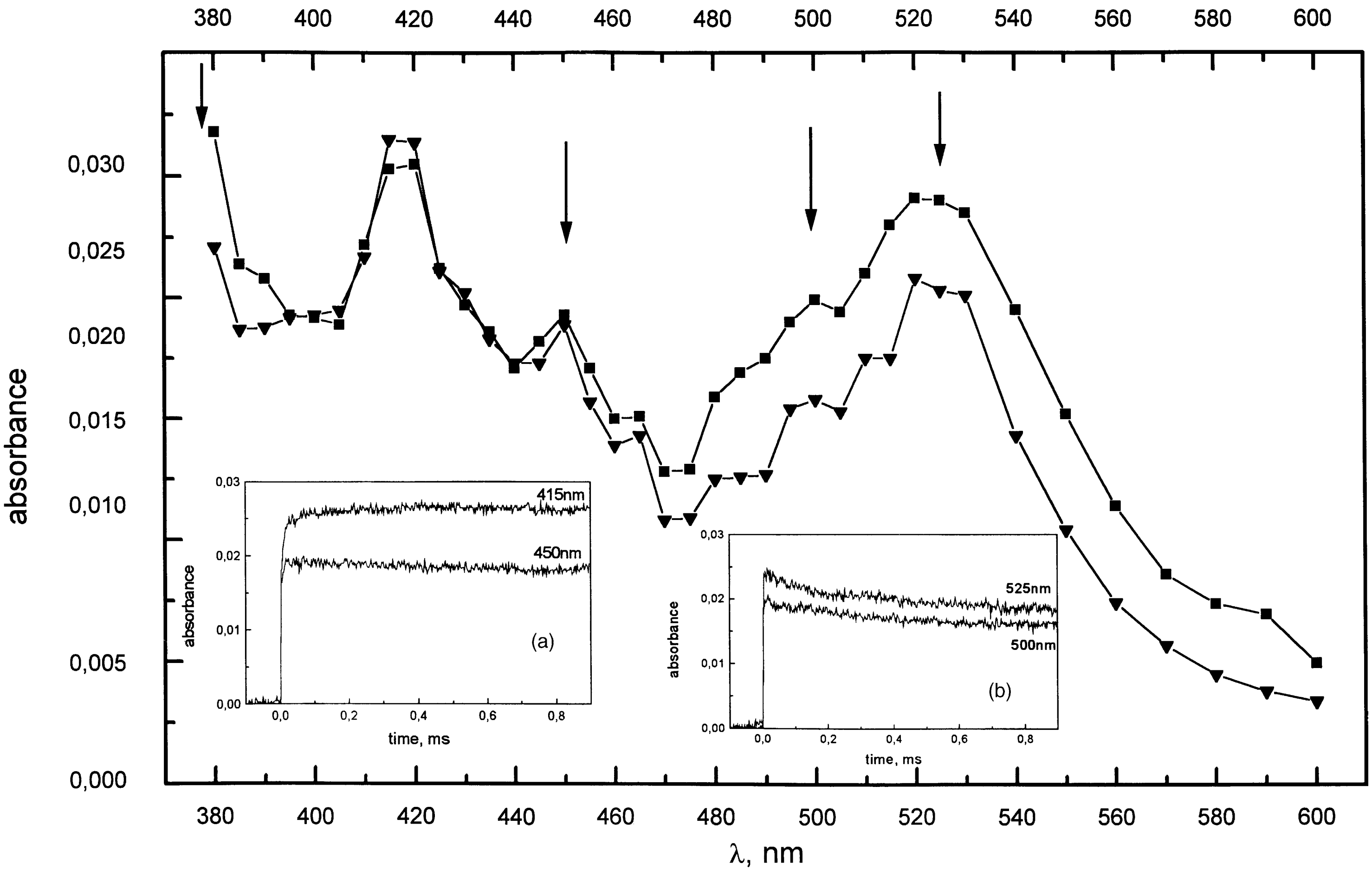

Fig. 4. Transient absorption spectra of pulse irradiated PET–Py film (450 μm thickness), [Py] ~ 1.3×10^{-1} mol dm^{-3} taken 20 μs (■) and 900 μs (▼) after the 1 μs pulse at 100 K. Inserts: absorption time profiles measured at 415 and 450 nm (a) and 500 and 525 nm (b).

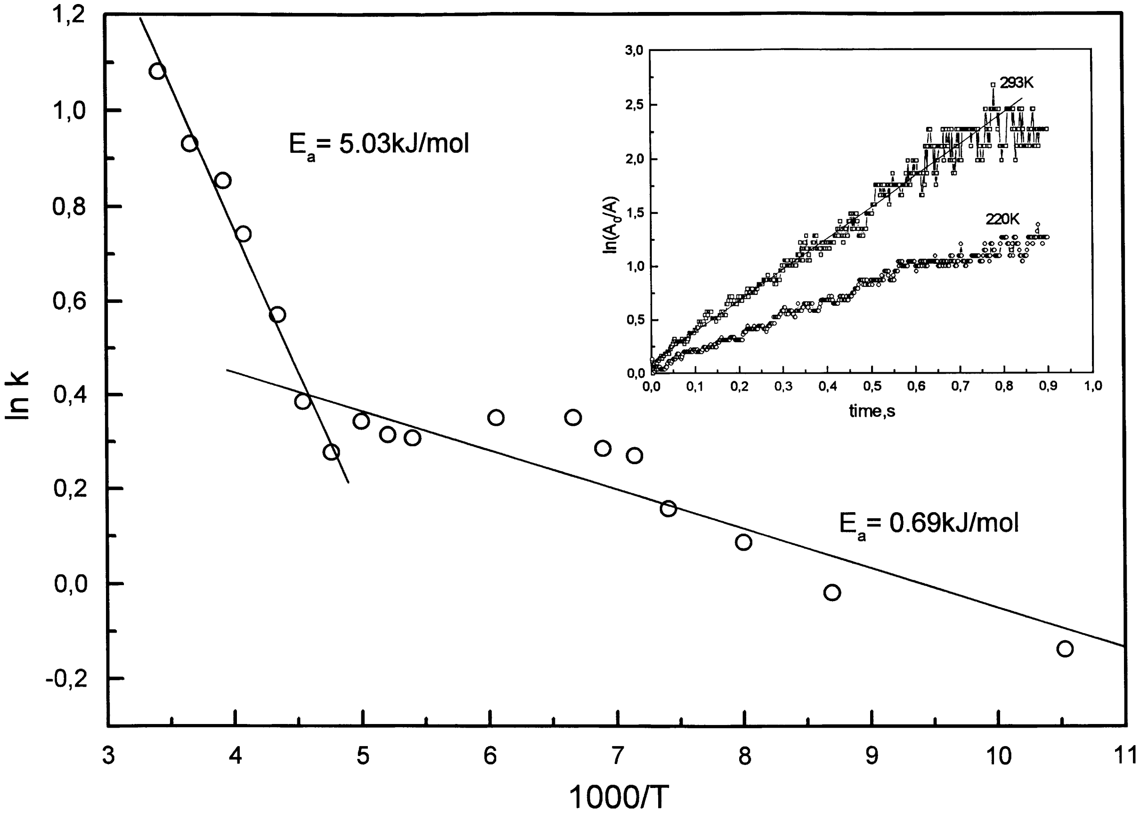

Fig. 5. The Arrhenius dependence for ^{3}Py* decay in PET–Py ([Py] ∼ 1.3×10^{-1} mol dm^{-3}) system (440 μm thickness) measured at 415 nm, 1 μs pulse. Insert: decay of absorption at 415 nm fitted to a first-order kinetic.

3.3. *Mechanism of ionic reactions in irradiated Py doped PET*

Mobile charges generated in the primary step of ionizing radiation interaction in PET matrix can produce PET radical ions, i.e. PET$^{\bullet-}$ and PET$^{\bullet+}$ [16] (Figs. 1, 2 and 4).

In the presence of Py molecules, in particular for high Py concentration (1.3×10^{-1} mol dm^{-3}) where aggregation seems to be possible, acceptor molecules may directly scavenge charges creating Py radical ions, Py$^{\bullet+}$ and Py$^{\bullet-}$. But mainly, Py$^{\bullet+}$ radical ions can be generated due to positive charge transfer process (1):

$$\mathrm{PET}^{\bullet+} + \mathrm{Py} \rightarrow \mathrm{Py}^{\bullet+} + \mathrm{PET} \qquad (1)$$

The absorption band of Py$^{\bullet+}$ (∼450 nm) was found during steady state as well as pulse radiolysis experiments (Figs. 1, 2 and 4). No convincing evidence was found supporting the formation of Py$^{\bullet-}$ radical anion in charge transfer reaction (2):

$$\mathrm{PET}^{\bullet-} + \mathrm{Py} \rightarrow \mathrm{Py}^{\bullet-} + \mathrm{PET} \qquad (2)$$

As it was mentioned earlier, such reaction seems to be unfavourable because of energy effects. In long time scale the absence of Py$^{\bullet-}$ radical ions seems to be evident (Fig. 2). Some close ionic pairs (Py$^{\bullet+}$ + Py$^{\bullet-}$) directly generated in high Py content PET matrix due to aggregation effect may recombine giving mainly excimer emission (Fig. 3A).

Radical ions Py$^{\bullet+}$ and PET$^{\bullet-}$ can recombine giving Py triplets (Fig. 3A, phosphorescence band, Fig. 4, 415–420 nm absorption band). The Py phosphorescence emission was detected during long time scale experiments in temperatures <200 K (Fig. 3).

In temperatures above 200 K, the ^{3}Py* absorption decay was observed (Fig. 5) but phosphorescence was not detected there (Fig. 3). Probably, matrix relaxation makes possible additional channel of ^{3}Py* decay. The activation energy equal to ∼5.98 kJ mol^{-1} was estimated for non-radiative decay mode of aromatic triplets in PMMA matrix [36] which is very close to the value (5.03 kJ mol^{-1}) found by us. One might take into account long-distance electron transfer from ^{3}Py* as non-radiative decay mode of ^{3}Py* as it was observed in rigid solutions of phthalic anhydride at 77 K [37,38].

4. Summary

- The strong correlation between the decay of ionic species (matrix and Py ones) and WS RTL results were found.
- The relaxation phenomena in PET matrix stimulated the behaviour of the radiation induced transient species (matrix and Py ones) there.
- In the polymer matrix under consideration the long lived Py radical cations were observed.

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